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**POWDER CONTAINING 2H-TYPE SILICON CARBIDE PRODUCED BY  
REACTING SILICON DIOXIDE AND CARBON POWDER IN NITROGEN  
ATMOSPHERE IN THE PRESENCE OF ALUMINUM**

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Translation of Japanese Kokai Patent No. 58-49611;  
Published, March 23, 1983; Application No. 56-144758; Filing  
Date, September 16, 1981;  
Assignee, Tokuyama Soda Co. Ltd., Tokuyama-shi, Japan

(NASA-TM-77597) POWDER CONTAINING 2H-TYPE  
SILICON CARBIDE PRODUCED BY REACTING SILICON  
DIOXIDE AND CARBON POWDER IN NITROGEN  
ATMOSPHERE IN THE PRESENCE OF ALUMINUM  
(National Aeronautics and Space

N85-10167

Unclas

G3/26 24183



NATIONAL AERONAUTICS AND SPACE ADMINISTRATION  
WASHINGTON, D. C. 20546      AUGUST 1984

1. Name of the invention

\* /53

Powder containing 2H-type silicon carbide produced by reacting silicon dioxide and carbon powder in nitrogen atmosphere in the presence of aluminum

2. Scope of the patent application

(1) Powder which contains silicon carbide consisting mainly of 40 % in volume of 2H-type silicon carbide,  $\beta$ -type silicon carbide and less than 3 % in weight of nitrogen.

(2) The method to produce powder containing 40 % in volume of 2H-type silicon carbide in which the reaction temperature is set at 1550 degrees C in an atmosphere of aluminum or aluminum compounds and nitrogen gas or an anti-oxidation atmosphere containing nitrogen gas.

(3) The method listed in para 2 (2) in which the mixture ratio of silicon dioxide and carbon powder is 0.55 - 1 : 2.0.

(4) The method listed in para 2 (2) in which the content of aluminum or aluminum compounds within silicon dioxide is less than 3 % in volume.

3. Detailed description of the invention

This invention introduces the method to produce powder containing the new 2H-type silicon carbide. To be more precise, the method to produce powder containing more than 40 % in volume of 2H-type silicon carbide which is consisted of mainly 2H-type silicon carbide,  $\beta$ -type silicon carbide and less than 3 % in weight of nitrogen.

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\* Numbers in the margin indicate pagination in the foreign text.

In the past,  $\alpha$  and  $\beta$ -type silicon carbide was widely used to produce ceramics of an excellent quality. However, these silicon carbide products had a deficiency in its high sintering temperature. The emergence of the 2H-type silicon carbide which has a low sintering temperature has been expected. Yet, in spite of the fact that the 2H-type silicon carbide is widely known, the production of powder which contains a high level of the 2H-type silicon carbide had been difficult; particularly, the technology of industrial production of high quality 2H-type silicon carbide has not been developed yet. For example, a proposal has been made to produce silicon carbide powder rich in 2H-type silicon carbide by reacting silicon dioxide and carbon powder in an atmosphere with a relatively large volume of aluminum at 1200 - 1500 degrees C temperature under reduced pressure according to the Kokai Patent Application #54-121298. Although this is an improved method compared to the traditional production methods, it requires decompression procedures and the production method does not meet the industrial requirements due mainly to its low production rate. In addition, it is not the ideal product because of its high ratio of aluminum content. /54

In order to correct the above deficiencies of the previous invention, this invention was completed after a period of intensive studies. It has been revealed that by reacting silicon carbide and carbon powder in an atmosphere of nitrogen gas that contains aluminum at 1550 degrees C or higher temperature, silicon carbide powder rich in 2H-type silicon carbide can be produced.

This invention, in other words, is the powder which contains

more than 40 % in volume of 2H-type silicon carbide,  $\beta$ -type silicon carbide and less than 3 % in weight of nitrogen. This invention also provides the method to produce silicon carbide powder which contains more than 40 % in volume of 2H-type silicon carbide in an atmosphere which consists of aluminum or aluminum compounds and an atmosphere of anti-oxidation containing nitrogen gas at 1550 degrees C temperature.

Silicon carbide in this invention contains 40 - 50 % in volume of 2H-type silicon carbide, and is silicon carbide in powder form consisting mainly of 2H-type silicon carbide and  $\beta$ -type silicon carbide. Also, silicon carbide in this invention contains the element, rooted to the production method, which is 3 % in volume of nitrogen. Many reports have been made in the past including including the above mentioned Kokai Patent Publication #54-121298 concerning the production method of less than 40 % in volume of 2H-type silicon carbide. This is the first invention that enabled the production of 2H-type silicon carbide with the content ratio of 40, 50, or even 60 %. Moreover, in this invention, it is necessary that the content of nitrogen be less than 3 % in weight, preferably 0.01 - 2.0 % in weight. This is a new invention. It is not necessarily clear as to how and in what format nitrogen is contained in silicon carbide, or how nitrogen influences the nature and composition of silicon carbide. However, considering the following merits of silicon carbide by this invention as compared to the previous silicon carbide it is assumed that these merits have something to do with the construction of the substance. Sintering substance by this invention that is obtained by 10

minutes of hot pressing have a flex rigidity of more than 50 Kg/mm<sup>2</sup> at 1500 degrees C. This is a drastic improvement compared to the previous silicon carbide sintering containing 2H-type silicon carbide which has a high aluminum content rate resulting in the lowering of a flex rigidity in high temperatures. Although it has been known that 2H-type silicon carbide is stable under 1500 degrees C temperature but starts to generate  $\beta$ -type silicon carbide above 1500 C, the 2H-type silicon carbide by this invention is stable at 1500 C, 1550 C, 1575 C and even above 1600 C. The difference is not only because of its superior purity but also nitrogen components within the silicon carbide which may have something to do with the difference.

Up to this date, it is not clear how nitrogen is formed within silicon carbide. When an attempt is made to produce silicon carbide using the method of this invention under 1500 C temperature, nitrogen content within silicon carbide in the form of silicon nitride ( $\text{Si}_3\text{N}_4$ ) exceeds 30 % in weight, however, as the temperature is raised to 1550 C or 1600 C the nitrogen content becomes extremely low, so low that the existence cannot be confirmed even by X ray diffraction. Judging from the advantages mentioned earlier, it is assumed that nitrogen is not in the form of silicon nitride but it either acts similar to aluminum during the formation of 2H-type silicon carbide or it triggers the reaction agents and stays as is within silicon carbide. Yet, the lowest content of nitrogen within silicon carbide, if the purity is at issue, is the most desirable; in case of industrial production of silicon carbide, the content should be 0.05 - 1.5 % in weight.

Silicon carbide by this invention mainly consists of more than 40 % in volume of 2H-type silicon carbide and  $\beta$ -type silicon carbide as mentioned earlier; the content of aluminum used as if it were a catalyzer in the process of the production could reach the maximum of 4.0 % in weight occasionally. Therefore, aluminum is contained as one of impurities during the production process; as long as the content does not bring about a negative influence toward normal generation of 2H-type silicon carbide, it is desirable to keep the content as low as possible. In the case of obtaining silicon carbide through normal procedures, the content generally ranges between 0.01 - 1.5 % in weight.

Silicon carbide by this invention can be in the composition as mentioned earlier, and its production method is not limited to one. The following are the examples of production methods generally used:

One of the raw materials for the production of silicon carbide by this invention is silicon dioxide. Silicon dioxide can be the same raw material as the one used for the production of silicon nitride and silicon carbide. Generally, amorphous silicon dioxide such as hydrated silicic acid or anhydrous silicic acid is suitable. In case crystalline silicon dioxide such as quartz are used, they need to be reduced to powder by crushing. Needless to say, amorphous silicon dioxide is usually powdery, ready for use as is, while cohesion particles should be mechanically broken up to less than 10 microns in size.

The other raw material in producing silicon carbide by the method of this invention is carbon powder. Any carbon, as long as

it is in powder form, can be used. Its suitable size is below 10 microns. The size of silicon carbide particle seems to be influenced by the size of carbon powder. Therefore, in order to produce silicon carbide in a fine powder form, the raw material, carbon powder, also needs to be in a fine powder form. Generally, carbon black seems to be the best carbon powder material for industrial use. As these two raw materials, silicon dioxide and carbon powder, are mixed together, the ratio must be just right. If one is extremely heavy in volume, the material which did not undertake chemical reactions is mixed in silicon carbide as is, making it possible to extract. As a result, the finished product, silicon carbide, becomes contaminated with impurities. For the reason cited, the mixture of raw material must be even handed. For industrial use, the mixture of silicon dioxide and carbon should be 1 : 0.55 - 2.0 ratio, preferably 1 : 0.6 - 1/0 ratio.

In the process of chemical reactions to obtain silicon carbide using the method of this invention, aluminum compounds such as aluminum, alumina, aluminum nitrate and aluminum sulfate are required as reactants. In the absence of these aluminum reactants, far less than 40 % in volume of 2H-type silicon carbide is produced. Yet, since these aluminum reactants are not the purpose but means to the finished products, they must be used in correct volume. If not, aluminum compounds will remain in the finished product, silicon carbide, and they cannot be separated from silicon carbide once chemical reaction is completed. Therefore, in producing silicon carbide using the method of this invention, the content of aluminum in silicon dioxide should be less than 3 % in



weight. For industrial use, the same ratio should be 0.01 - 2 % in 156 weight.

The reaction to obtain silicon carbide, in addition to what has been described above, needs to be processed in nitrogen gas atmosphere or an anti-oxidation atmosphere that contains nitrogen gas, eg. nitrogen and argon, neon, helium...etc. The volume of nitrogen gas must be at the minimum equal to the volume of nitrogen contained in silicon carbide. Yet, the use of too much nitrogen gas must be avoided because it will result in generation of silicon nitride. The cause of silicon nitride is not limited to the excessive use of nitrogen gas - chemical reaction device, reaction conditions, kind of raw material and other factors could also cause the generation of silicon nitride. The standard for the volume to be used in the case of batch reaction should be 5 - 6 % more nitrogen gas than the volume of nitrogen gas contained in silicon carbide.

The reaction temperature in the process of silicon carbide production is another important condition. In the case of reaction process - the process to produce a large amount of 2H-type silicon carbide by the reaction of silicon dioxide and carbon powder - the reaction temperature must be above 1550 C, preferably 1575 C or even 1600. Yet, the temperature shouldn't be too high since extremely high temperature causes 2H-type silicon carbide to change to  $\alpha$ -type silicon carbide. The temperature to change the 2H-type to  $\alpha$ -type cannot be correctly determined since it tends to be different by the reaction condition and composition and kind of the raw material. Generally speaking, the temperatures below 1825 - 1800

are the standard. Also, the time of the reaction can be between 30 minutes to 10 hours.

As mentioned earlier, the production method of silicon carbide by this invention involves silicon dioxide, carbon powder and aluminum or aluminum compounds in an atmosphere which contains nitrogen gas or an anti-oxidation atmosphere containing nitrogen gas at a fixed temperature. Aluminum or aluminum compounds do not necessarily have to be used separately with silicon dioxide and carbon powder. Because the amount of aluminum needed by this invention is so little, the raw material, silicon dioxide which contains a small amount of aluminum, at the time of silicon carbide production can be used as the source of both silicon dioxide and aluminum.

In case silicon carbide is produced by the method of this invention, as shown in the practical application to be shown later, silicon carbide which contains 2H-type silicon carbide is obtained at the ratio of 70 % in volume or more of the total silicon carbide. In addition, contrary to the traditional belief that 2H-type silicon carbide produced at the temperature above is unstable, stable 2H-type silicon carbide is produced at the temperature of 1600 C or above. This is an amazing, totally unexpected phenomenon.

Also, silicon carbide powder consisting of 40 % in volume of 2H-type silicon carbide, consisting mainly of 2H-type silicon carbide and  $\beta$ -type silicon carbide and below 3 % in weight of nitrogen is produced at the temperature 100 to 200 degrees lower than the previous methods. In addition, the rigidity of the

finished product at higher temperature is superb. Therefore, the /57  
benefit of this invention is not limited in the area of new  
ceramics. It can be used in many other areas.

The following are the practical applications of this  
invention. The applications are not limited to those listed below.

#### Application #1

500 cc silicic acid soda solution, 1 mol/l, ( $\text{SiO}_2/\text{Na}_2\text{O}$   
molarity 2.0) was mixed with 250 cc calcium chloride solution, 0.5  
mol/l. The mixed solution was sealed under 200 degrees C  
temperature and 0.5 Kg/cm<sup>2</sup> for 20 hours. After cooling, filtering  
and drying, a powdery substance whitish in color was obtained. A  
chemical analysis indicated that the whitish powder was of a  
composition close to  $3\text{Na}_2\text{O} \cdot 0.9\text{CaO} \cdot 32\text{SiO}_2 \cdot 25\text{H}_2\text{O}$ . Under the  
microscopic observation, square flakes approximately 5 microns in  
size were observed. The powder was mixed in 1 N HCl and agitated  
for two hours at 50 degrees C temperature. After filtering and  
drying the flakes were found to be silica. As the impurities of  
silica were analyzed, they were found to be Al, 1.6 % in weight,  
Ca, 0.03 % in weight and Fe, 0.002 % in weight.

Silica and carbon black were mixed at the weight ratio of 1 :  
1, placed in a graphite crucible which was placed in a furnace  
tube, 60 mm in diameter. The crucible was heated at 1700 C  
temperature for 5 hours; nitrogen gas was introduced to the furnace  
tube at the rate of 20 cc/ min. After heating, excess carbon was  
burned off in the air by 650 degrees C heat. The chemical analysis  
of the powder produced indicated the content of 27.0 % in weight of  
carbon and 0.6 % in weight of nitrogen. The X ray diffraction of

the powder revealed that the powder consisted of 2H-type and  $\beta$ -type silicon carbide. The assessment of the content of 2H-type silicon carbide was made by the Ceramic Industry Association magazine 87-11, page 576 (1979). By using the peak intensity of  $2\theta = 33.6^\circ$  and  $2\theta = 35.6^\circ$  by CuK $\alpha$  beam of the X ray diffraction, the following formula was established:

$$\text{Content of 2H-type (\%)} = 100R / (1 + R)$$

$$\text{Content of } \beta\text{-type (\%)} = 100 / (1 + R)$$

$$R = 2.53I / (100 - 0.668I), I = 100 \times \text{the ratio of}$$

$$2\theta = 35.6^\circ (\text{peak intensity}) : 2\theta = 33.6^\circ (\text{peak intensity})$$

Based on the above figures, the powder was found to consist of 79 % in volume of 2H-type, and 21 % in volume of  $\beta$ -type.

#### Application #2

The same experimentation as the application #1 using the same silica used in the experimentation #1 and silica with a different Al content was conducted. The result is shown in Fig. 1. No. 6 and 7 are comparisons.

#### Application #3

Silica anhydride obtained by the hydrolysis of silicon tetrachloride (commercial brand, Aerosil), carbon black and alumina (purity 99.9 %, average grain diameter 0.7 microns) in the weight ratio of 1 : 0.7 : 0.03 were placed in a graphite crucible, which was placed in a furnace tube, diameter 60 mm. The crucible was heated at 1700 C temperature for 5 hours as nitrogen gas was introduced to the tube at the rate of 50 cc/min. The excess carbon was removed by applying 650 C temperature in the air. The chemical analysis of the powder revealed 26.8 % in weight of carbon and 0.6

% in weight of nitrogen. The result of X ray diffraction revealed 53 % in volume of 2H-type and 47 % in volume of  $\beta$ -type.

#### Application #4

The same experimentation as the application #3 was conducted using aluminum or aluminum compound as the source of aluminum. The result is shown in Fig. 2. No. 5 indicates a comparison.

#### Application #5

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Silicon carbide powder consisting of 2H-type silicon carbide, 79 % in volume and  $\beta$ -type silicon carbide, 21 % in volume were fluorinated at 80 degrees C temperature; silica was removed, then, washed and dried. This powder was added with boracic acid, 1 %, and carbon, 1 %, placed in a graphite mold, 40 mm in diameter, and hot pressed at 200 Kg/cm<sup>2</sup> in 2000 C temperature for 10 minutes in argon atmosphere. The density of the sintering was 3.17 g/cm<sup>3</sup>. The sintering was cut to an experimental material, 3 mm in thickness and 4 mm in width. The flex rigidity in high temperatures of this test material was measured at 1500 c temperature in argon atmosphere. The four test material indicated the average rigidity of 63 Kg/mm<sup>2</sup>.

Assignee: Tokuyama Soda Co., Ltd.

Amendment dated February 5, 1982

To: Director, Patent Office ATTN: Haruki Shimada

1. Indication of the item: 56-144758

2. Name of the invention: Powder containing 2H-type

**silicon carbide produced by reacting silicon dioxide and carbon powder in nitrogen atmosphere in the presence of aluminum.**

**3. Name of the applicant:**

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**4. Date of the amendment: January 5, 1982**

**Date sent forward: January 26, 1982**

**5. Additional invention listed in the amendment: none**

**6. Amendment concerning: Application and details.**

**7. Contents of the amendment:**

**(1) Application is changed as indicated in the attached papers.**

**(2) The details are changed to the typed papers which are attached.**

KEY LIST:

FIG. 1

- a. aluminum content within silica ( % in weight)
- b. atmosphere (gas) (volume)
- c. sintering temperature (C)
- d. composition
- e. 2H-type ( % in volume)
- f. nitrogen ( % in weight)

Fig. 2

- g. Al or Al compound
- h. Al added to silica ( % in weight)
- i. composition

Fig. 1

第 1 表

No.	B の Al 含有量 (重量%)	雰囲気ガス (体積%)	焼成温度 (℃)	d 組成	
				e 体積%	f 重量%
1	1.6	Ar (20%)	1600	75	1.5
2	"	"	1750	78	0.6
3	0.5	"	"	61	0.5
4	"	"	1700	64	1.0
5	0.05	"	"	50	0.8
6	1.6	"	1500	—	34.7
7	"	Ar (12%)	1700	16	0.0

(17)

Fig. 2

第 2 表

No.	g は Al 化合物	h 対する Al 添加量 (重量%)	i 組成	
			j 体積%	k 重量%
1	アルミニウム	1.0	51	0.5
2	シリカアルミナ	0.8	49	0.9
3	モルブナイト	1.6	45	1.0
4	硫酸アルミニウム	0.6	49	0.7
5	無添加	0.0	15	0.7

- j. 2H-type ( % in volume)
- k. nitrogen ( % in weight)
- 1. aluminum                      2. silica alumina
- 3. mordenite                    4. aluminum sulfate
- 5. no additives